# Topic E – Enviro Chemistry Part 10 – Smog for HL

IB Chemistry

Topic E – Enviro

Hodder Ed - Talbot

# Smog – 2hrs

- E.10.1 State the source of primary pollutants and the conditions necessary for the formation of photochemical smog. (1)
- E.10.2 Outline the formation of secondary pollutants in photochemical smog. (2)

# E10.1 – Formation of Smog

- E.10.1 **State** the source of primary pollutants and the conditions necessary for the formation of photochemical smog. (1) *VOCs and NOx, temperature inversion, windlessness and bowl-shaped cities should be discussed.*
- Originally **smog** referred to fog-like covering that fell over cities due to large amounts of smoke and $SO_2$ from the burning of coal.
- Today, the term generally refers to **photochemical smog** in which primary pollutants derived from vehicle traffic undergo a series of light-driven chemical reactions forming toxic compounds

# E10.1 – Primary, Secondary Pollutants

- Cities that experience intense photochemical smog include Athens, Hong Kong, Houston, Los Angeles, Mexico City, Sao Paulo, and Tehran.
- Photochemical Smog
  - Primary Pollutants:
    - $No_x$($NO$ + $NO_2$), VOC's, CO, particulate matter
  - Secondary Pollutants:
    - $O_2$, $NO_2$, $H_2O_2$, PAN (peroxyacetyl nitrate), partially oxidized VOC's, $HNO_3$, particulate matter

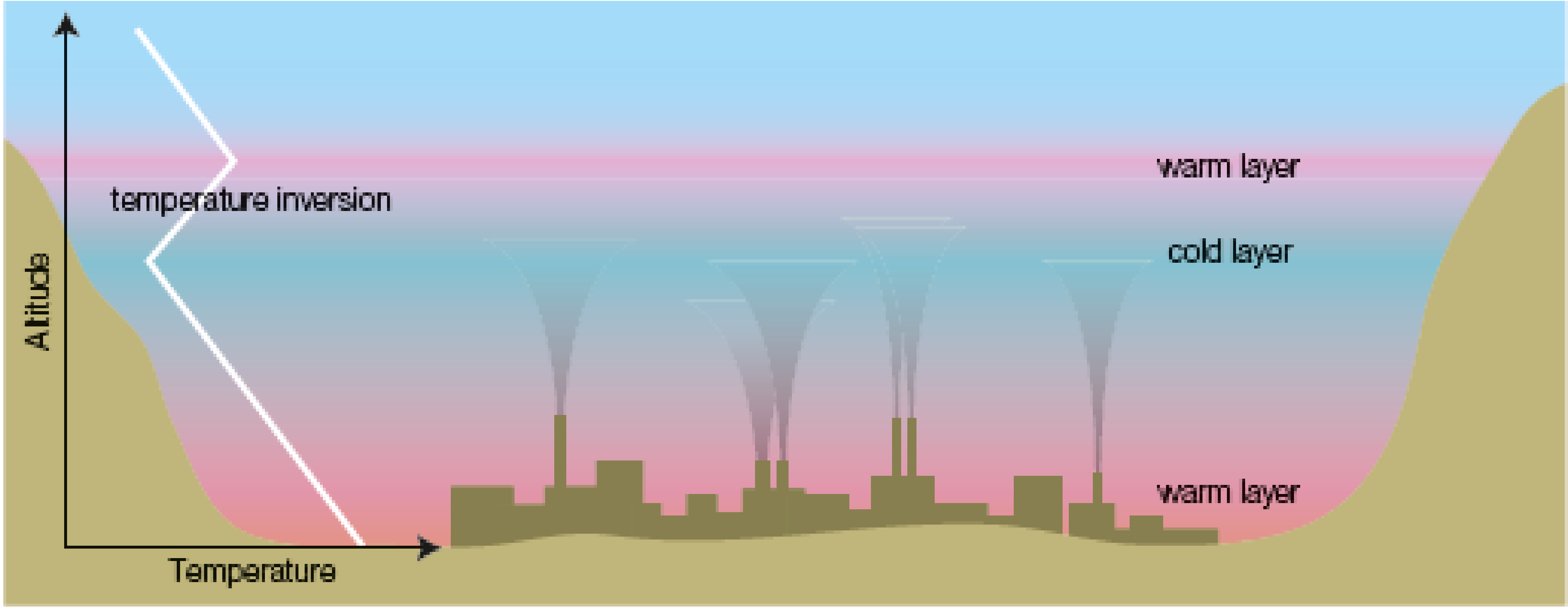
| Characteristic | Secondary smog | Primary smog |
|---|---|---|
| Air temperature | 24–32 °C | –1 to 4 °C |
| Relative humidity | <70% | 85% (and fog) |
| Wind speed | Slow | Calm |
| Inversion height | –1000 m (Los Angeles) | –100 m |
| Visibility | < 800 m and 1600 m | < 30 m |
| Months of most frequent occurrence | July to September | December to January |
| Major fuels | Petrol | Coal |
| Principal constituents | Ozone, nitrogen monoxide, nitrogen dioxide, carbon monoxide and organic matter, peroxyacyl nitrates (PANs) and particulate matter | Particulate matter, carbon monoxide, sulfur compounds |
| Type of chemical reaction | Oxidizing | Reducing |
| Time of maximum occurrence | Midday | Early morning |
| Principal health effects | Temporary eye irritation (PAN); respiratory system (ozone, secondary organic aerosol) and cardiovascular system | Bronchial irritation, coughing (sulfur dioxide/smoke) |
| Materials damaged | Rubber cracked (ozone) | Iron, concrete |

**Table 25.6** Comparison of primary and secondary smogs

# E10.1 – Conditions Leading to Photochemical Smog

- The primary pollutants leading to photochemical smog are **NO** and **VOC's** from vehicle exhausts
  - $N_2 + O_2 \rightarrow 2NO\bullet$
- Geographical location such as L.A. and Mexico City both located in-between mountains for a geological 'bowl' or 'basin'
- These cities also have **inversion layers** (temperature inversion) in which the air close to the ground is colder than the above which prevents the polluted air from the city from rising
  - The build-up of pollutants are then acted upon by sunlight

# E10.1 – Temperature Inversion



# E10.2 – Formation of Smog Pollutants

- E.10.2 Outline the formation of secondary pollutants in photochemical smog. (2) *Examples include $NO_2$, $O_3$, aldehydes and peroxyacylnitrates (PANs). The role of free radicals and sunlight should be emphasized.* ***Aim 7:*** *Three-dimensional and four-dimensional GIS techniques and data banks can be used.*
- Harmful substances from photochemical smog include $NO_2$, $O_3$, aldehydes (HCHO), peroxyethanoyl nitrate (PAN's), and secondary aerosol particles (comprised of sulfates, nitrates and oxidized organic compounds).
  - All from free-radical processes driven by the sun

# E10.2 – Formation of $NO_2$ and Ozone

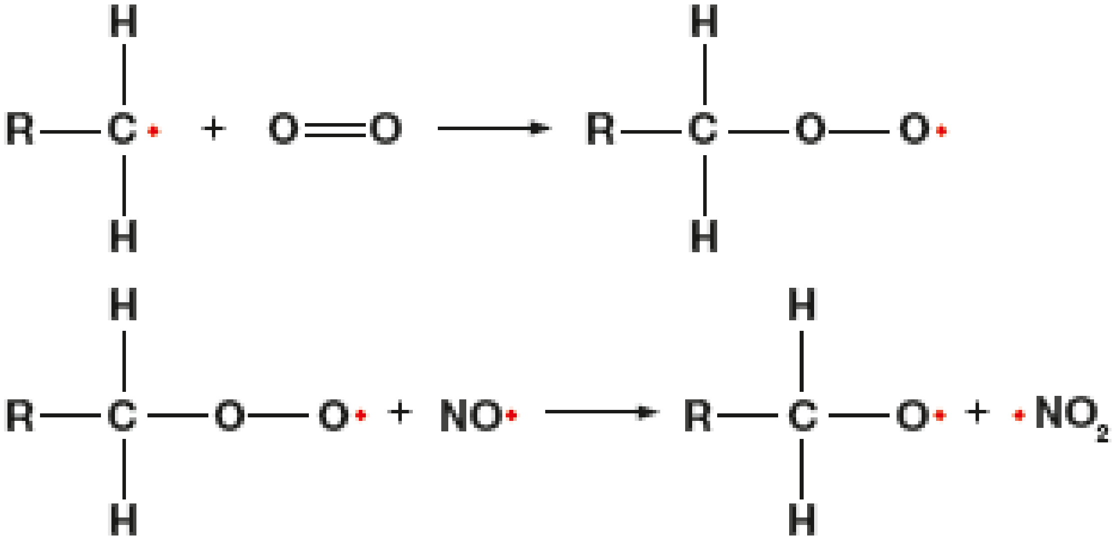
- Formation of $NO_2$
  - $2NO\bullet + O_2 \rightarrow NO_2$
- Formation of ozone
  - $NO_2\bullet$ + UV (430nm) $\rightarrow NO\bullet + O\bullet$
  - $O\bullet + O_2 + M \rightarrow O_3 + M$
  - $NO\bullet + O_3 \rightarrow NO_2\bullet + O_2$
- If these were the only processes involved, then a steady state would be reached, with ozone depletion/formation stable. **BUT,** further processes allow **NO to re-oxidize to $NO_2$** without depleting ozone. More ozone created than destroyed = **ozone build up**!

# E10.2 – Formation of Alkyl Radical

- A proposed mechanism for this re-oxidation involves hydroxyl radicals and hydrocarbons.
- The hydroxyl radical, HO•, is generated by the reaction of excited oxygen atoms (O•*) with water
- These are then formed from the photodissociation of ozone.
  - $O_3$ + UV (290-320nm) → $O_2$ + O•*
  - O•* + $H_2O$ → 2HO•
- Hydroxyl radicals combine with hydrocarbons, RH (like VOC's) leading to the formation of alkyl radical
  - $RCH_3$ + OH• → $RCH_2$• + $H_2O$

# E10.2 – Formation of $NO_2$ Radical

- The organic free-radicals combine with dioxygen, $O_2$, forming organic peroxy radicals, $RCH_2O_2\bullet$
- These radicals are able to oxidize NO to $NO_2$
  - $RCH_2\bullet + O_2 \rightarrow RCH_2O_2\bullet$
  - $RCH_2O_2\bullet + NO\bullet \rightarrow RCH_2O\bullet + NO_2\bullet$



# E10.2 – Complete production of $O_3$

- The resulting $RCH_2O\bullet$ radicals can react with di-oxygen molecules to form aldehydes, RCHO :
  - $RCH_2O\bullet + O_2 \rightarrow RCHO + HO_2$
  - $\bullet HO_2 + NO\bullet \rightarrow HO\bullet + \bullet NO_2$
- These radicals convert NO to $NO_2$, which then photolyzes to form ozone
  - $\bullet OH + RCH_3 + 2O_2 + 2NO\bullet \rightarrow H_2O + RCHO + 2NO_2\bullet + \bullet OH$
- Combined with
  - $2NO_2 + 2hf + 2O_2 \rightarrow 2NO\bullet + 2O_3$
- Results in:
  - $OH + RCH_3$ (need $NO + O_2$) $\rightarrow H_2O + RCHO + 2O_3 + \bullet OH$

# E10.2 – Daily Cycle of Pollutants

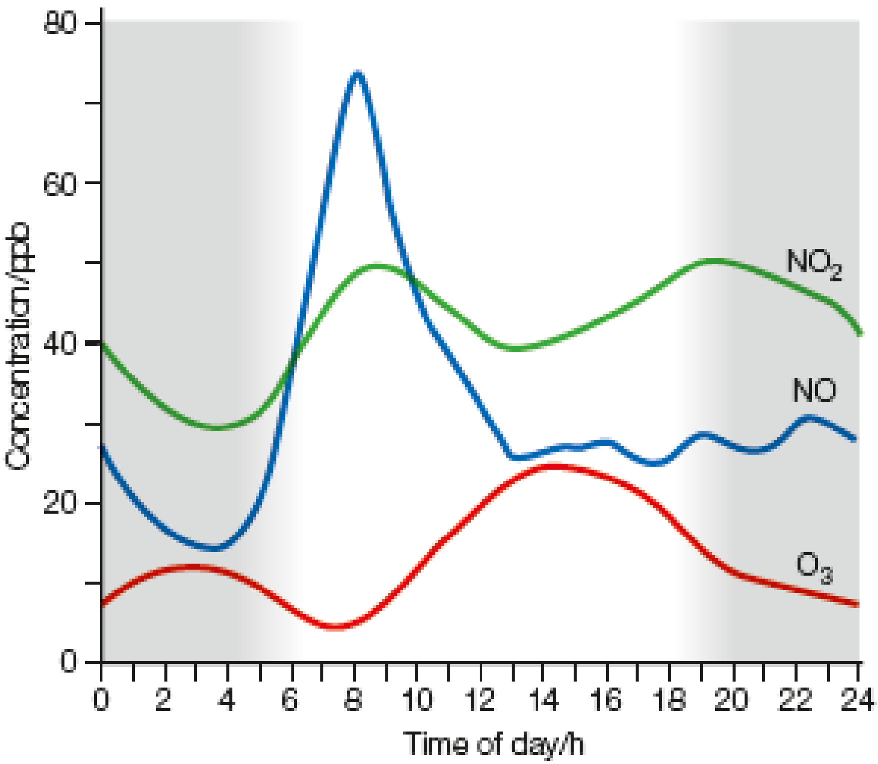



**Figure 25.37** Variation of the concentrations of ozone and oxides of nitrogen on a summer weekday in London

- Primary pollutant concentrations in polluted cities such as London are high early in the morning as rush hour → NO + $C_xH_Y$.
- Later $NO_2$ increases as NO is oxidized
- Driven by sunlight (most intense at noon)
- [Ozone] peaks after lunch when $NO_2$ generates O•* leading to ozone formation.
- In evening NO is replenished by rush hour depleting ozone more

# E10.2 – Harmful Effects of Ozone

- Contained within many synthetic materials, C=C can often be found.
  - These compounds are paints, dyes, and plastics
  - The addition of $O_3$ across this double bond can cause deterioration and color bleaching
  - Polymer chains in rubber tires could be broken down by ozone, causing them to crack and split
  - $O_3$ attacks green plants, discoloring their leaves and resulting in decreased photosynthesis

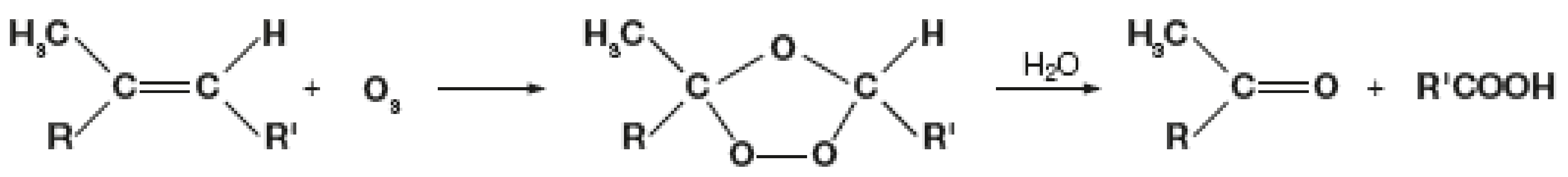


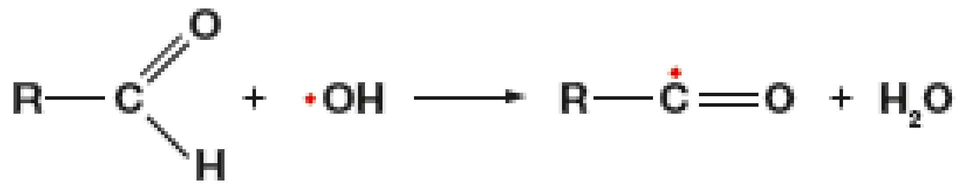

**Figure 25.38** The reaction between ozone and carbon–carbon double bonds

# E10.2 – Formation of PANs

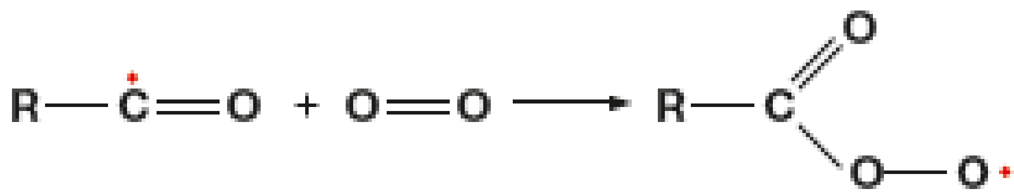
- Remember, PANs are harmful substances that results from photochemical smog
- As we have seen $NO_2$ shows up all over in $O_3$ formation equations
- $NO_2$ can be removed from the photochemical smog chain reaction by reaction with the PAN (peroxyacyl) radical. The resultant compound, peroxyacyl nitrate, has many adverse health effects

# E10.2 – PAN Compounds

- $RCHO + HO\bullet \rightarrow RCO\bullet + H_2O$

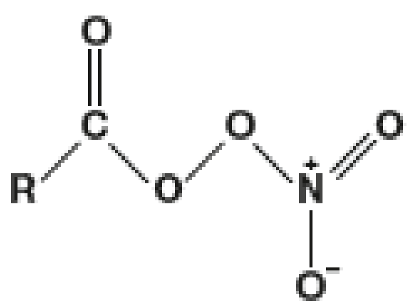


- $RCO\bullet + O_2 \rightarrow RC(O)O_2\bullet$



- $RC(O)O_2\bullet + NO_2\bullet \rightarrow RC(O)O_2NO_2$

This stable PAN compound can be transported elsewhere in the troposphere and slowly dissociate and each contributing to ozone elsewhere.



For the peroxyacyl nitrate molecule, the R group could represent ($-CH_3$) which results in a peroxyethanoyl nitrate which is toxic, irritates the eyes, and is damaging to green plants